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XPS Study of Superconducting LiTi$_2$O$_4$ and LiTi$_{2-x}$Cu$_x$O$_4$ Sol–Gel Derived Powders and Thin Films

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In this work X-ray photoelectron studies of lithium titanate and copper doped lithium titanate are presented. Both, powder and thin films samples were prepared by sol–gel method. After preparation, the samples were heated in argon atmosphere at various temperatures in a range from 500 °C to 600 °C for 20 h. The crystalline structure of the samples was investigated by X-ray diffraction, while the oxidation states of the elements were examined by X-ray photoelectron spectroscopy method. X-ray diffraction measurements confirmed spinel phase of all manufactured samples. However it is well known that electrical and superconducting properties of lithium titanate are strongly correlated not only with structure, but also with oxidation state of Ti ions. X-ray photoelectron spectroscopy investigations revealed mixture of Ti^{3+} and Ti^{4+} ions, although the Ti^{3+}/Ti^{4+} ratio is much smaller than $\frac{1}{2}$ needed for superconductivity. In this work dependence between calcination temperature as well as amount of Cu dopant and Ti^{3+}/Ti^{4+} proportion are reported.

1. Introduction

Lithium titanate Li$_{1+x}$Ti$_{2-x}$O$_4$ is an oxide spinel with a very interesting electrical properties related to average valence state of titanium ions. In turn, average valence state of titanium ions is directly correlated with composition. For the samples with composition $x = 0$, Li$^+$(Ti^{3+}Ti^{4+})O$_4$ material exhibits superconducting properties with a transition temperature $T_c = 13$ K. In this case average valence of Ti ions is equal to 3.5. It means that there is only one d electron for two titanium ions. Substitution of Ti ions by lithium leads to metal-semiconductor transition and lower critical temperature. For $x = 0.33$, Li$^+$(Ti$^+_{1/3}$Ti$^{4+}_{5/3}$)O$_4$, average valence of titanium reaches a value of 4, metal–insulator transition is observed and the system does not go into the superconducting state [1, 2]. In general, it may be possible that in lithium titanate, the change in the average valence of titanium ions in octahedral sites, dominates electrical properties (e.g. metal–semiconductor or metal–insulator transition). The change in average valence may be also caused by replacement of Ti ions by various elements. It was reported that in all the cases in which the substitution results in an increase of the valence of the titanium ions (e.g. doping by Cr, Al, Mg, Mn, or Cu), the transition from metallic to semiconductor behavior occurs at a titanium average valence of 3.60–3.64 [3]. Many scientific attention have been also devoted to the influence of Ti ions substitution on superconducting properties and critical temperatures of doped lithium titanate. It was found that doping by Al [4], B [5], Co [5], Cr [4, 7, 8], Ge, Mn [9], Ni [5] or V [5] ions have no effect in enhancement of T_c.

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Only Cu dopant gives hope to increase the transition temperature [3]. LiTi$_{2-x}$Cu$_x$O$_4$ samples that contained up to $x = 0.15$ were metallic and exhibited superconducting transition.

Lithium titanate is usually manufactured by solid state reaction method. There is only a little known about possibilities of preparation of lithium titanate with sol-gel route [10, 11], which has a great potential for many materials manufacturing. This chemical procedure allows to obtain materials with precisely controlled chemical composition. Additionally, in comparison with other methods, this one is relatively cheap, simple and does not require high vacuum equipment and high temperature [10, 12]. In this work X-ray photoelectron spectroscopy (XPS) studies of lithium titanate and copper doped lithium titanate prepared by sol–gel method are presented.

2. Experimental

For sol–gel synthesis lithium acetate dehydrate from Alfa Aesar and titanium(IV) butoxide 97% from Aldrich were used as reagents. Additionally, copper(II) nitrate from Alfa Aesar was used as a source of Cu dopant. Considering the easy evaporation of lithium ions during manufacturing and annealing process [13–15], lithium and titanium precursors were added in proper amount for obtained Li/Ti ratio equal to $\frac{1}{2}$, 2 and 3 in solution [16, 17]. Amount of copper precursor was calculated for LiTi$_{2-x}$Cu$_x$O$_4$ solution with an x index equal to 0.05. In the first step lithium acetate and copper nitrate was dissolved completely in ethanol using magnetic stirrer. After that titanium(IV) butoxide was added. Prepared sol was mixed by magnetic stirrer at room temperature for 10 min until it has transformed into homogeneous sol. To obtain thin films, the sol was deposited on a silica glass substrate by a spin coating technique at a rate

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of 100 rps. After that samples were dried at 100 °C for 20 h in argon atmosphere. Repeating the above procedure three times gave (after the subsequent annealing) approximately 450 nm thick films. The thickness of the samples was determined using profilometer. The films were finally calcinated in argon atmosphere for 20 h at 550 °C. To prepare xerogel powders, sol was left for seven days in air and room temperature to evaporate the solvent, subsequently dried and calcinated in the same conditions as the films. In a result of above procedure, obtained dark grey powder was compressed into pellets.

The structure of the samples was examined by X-ray diffraction (XRD) with Philips X'Pert diffractometer system. XRD patterns were taken at room temperature using Cu K_α radiation in a range of 10°–70° of 2θ.

XPS spectra were recorded with a multipurpose electron spectrometer PHI 5700/660 from Physical Electronics using monochromatized Al K_α radiation. The anode was operated at 15 kV and 225 W. Low and high resolution spectra were measured. The binding energies were corrected using the background C $1s$ line (285.0 eV) as a reference [18]. MultiPak program was used to fit high-resolution spectra. Mixed Gaussian and Lorentzian functions and Shirley background were applied.

3. Results and discussion

XRD patterns of manufactured films, when initial Li/Ti ratio was equal to $\frac{1}{2}$, 2 and 3 in solution are shown in Fig. 1. All investigated coatings revealed presence of lithium titanate spinel phase, but the best Li/Ti ratio for obtaining $Li_1Ti_2O_4$ spinel structure seems to be 2. Similar results were collected for powders. Also the sample doped with copper $LiTi_{2-x}Cu_xO_4$ ($x = 0.05$) exhibits pure lithium titanate spinel phase, due to successful substitution of Ti by Cu^{2+} ions.
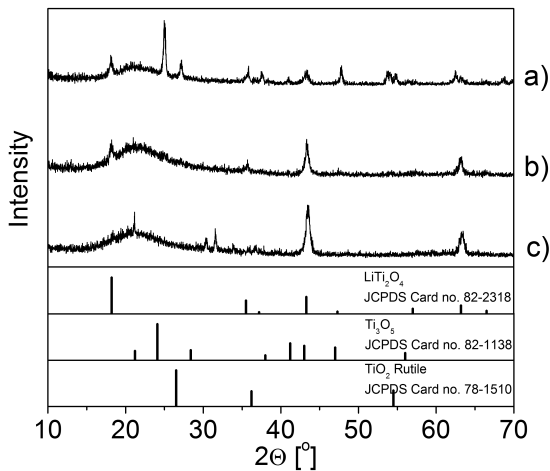

Fig. 1. XRD patterns of thin films, when initial Li/Ti ratio in solution was equal to (a) $\frac{1}{2}$, (b) 2 and (c) 3.

In Fig. 2a–c XPS spectra of $LiTi_2O_4$ films (Li/Ti initial ratio equal to 2) are presented. In O $1s$ region (Fig. 2a), apart from the peak in position 529.76 eV, reported to metal oxides, also peak at energy 531.68 eV is
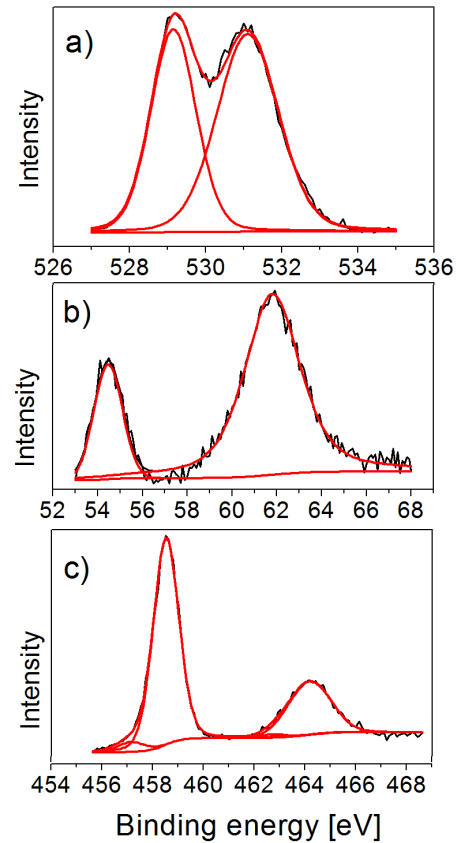

Fig. 2. XPS spectra of $LiTi_2O_4$ films (initial Li/Ti ratio equal to 2): (a) O $1s$ region, (b) Li $1s$ and Ti $3s$ regions, (c) Ti $2p$ region.

present. The last one may be attributed to H_2O rests, resulted from sol–gel preparation method. Figure 2b shows two peaks at energies 55.11 eV and 62.40 eV. The first one is associated to Li $1s$, whereas the higher energy peak corresponds to Ti $3s$. In presented in Fig. 2c Ti $2p$ region, two doublets are observed. The doublet at energies 458.55 eV (Ti $2p_{3/2}$) and 464.17 eV (Ti $2p_{1/2}$) is attributed to Ti^{4+} ions, the doublet at energies at 456.94 eV (Ti $2p_{3/2}$) and 462.94 eV (Ti $2p_{1/2}$) is associated to Ti^{3+} ions. Positions of these doublets are similar to those given in literature [19–21]. As it was mentioned previously, in spinel $LiTi_2O_4$ structure exhibiting superconducting properties, Ti^{3+}/Ti^{4+} ratio should be $\approx 1/2$.

In present $LiTi_2O_4$ films, this ratio is ≈ 0.047 and as it is seen in Fig. 3 increases with the increase of initial Li/Ti ratio. However, the reason for this increase is not clear. Usually Ti^{3+} ions are correlated with surface defects [19]. In the case of presented films, defects may be introduced together with an increased amount of lithium than that resulting from stoichiometry. Ti^{3+} ions are not seen in powder samples doped with copper ions $LiTi_{2-x}Cu_xO_4$ ($x = 0.05$) (Fig. 4a). This may be related to the substitution of copper ions in titanium positions. As it was shown by Faran et al. [3], Ti substitution by Cu ions results in an increase of the average valence of Ti
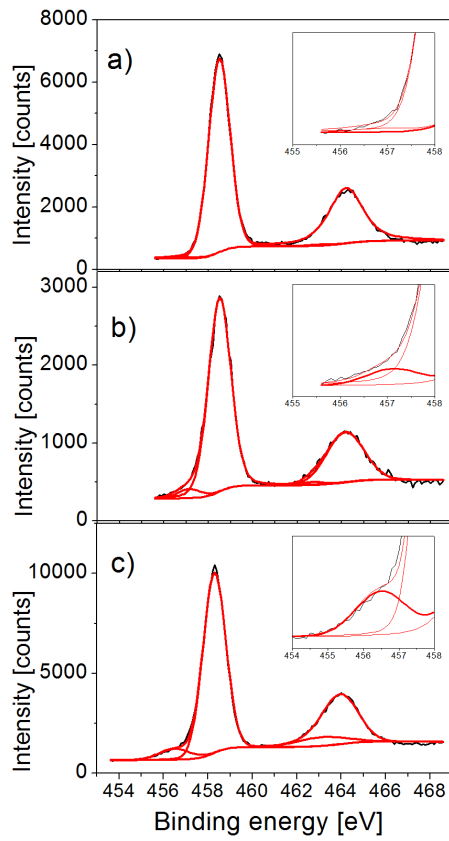
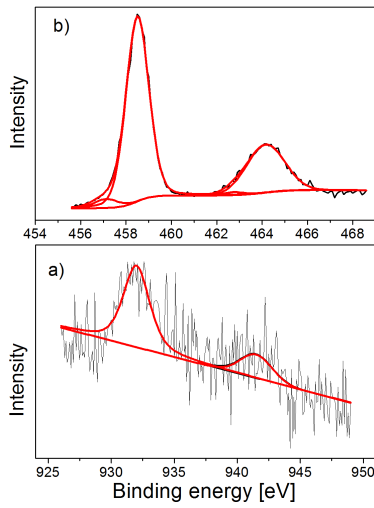Fig. 3.   Ti 2p spectra of LiTi$_2$O$_4$ films with the initial Li/Ti ratio (a) $\frac{1}{2}$, (b) 2, and (c) 3.

loss of their. Presence of copper ions in the samples is seen in Fig. 4b (Cu 2p region). Peaks at energy positions 932.00 eV and 941.50 eV are close to those reported for copper oxides, confirming successful substitution of Ti by Cu^{2+} ions.

Fig. 4.   XPS spectra of LiTi$_{2-x}$Cu$_x$O$_4$ ($x = 0.05$) powders (initial Li/Ti ratio equal to 2): (a) Ti 2p region, (b) Cu 2p region.

ions. So when the initial amount of Ti^{3+} ions in the samples was low, the doping by Cu ions could cause a total

4. Conclusions

Presented results show that proposed sol–gel method can be successfully used to produce lithium titanate and copper doped lithium titanate layers and powders. Observed in XPS studies Ti^{3+}/Ti^{4+} ratio increases in the samples with the increase of initial Li/Ti ratio, which can be correlated with defects introduced with higher (than stoichiometric) lithium quantity. Unfortunately, all the samples (films and bulk powders) exhibit lower Ti^{3+}/Ti^{4+} ratio than that is needed for superconductivity. The results obtained for Cu doped sample confirm successful substitution of Ti by Cu ions, although this substitution results in an increase of the average valence of Ti ions.

References

[1] D.C. Johnson, *J. Low Temp. Phys.* **25**, 145 (1976).

[2] M.A. Green, M. Dalton, K. Prassides, P. Day, D.A. Neumann, *J. Phys. Condens. Matter* **9**, 10855 (1997).

[3] O. Faran, V. Volterra, *Physica C* **255**, 329 (1995).

[4] P.M. Lambert, P.P. Edwards, M.R. Harrison, *J. Solid State Chem.* **89**, 345 (1990).

[5] O. Faran, V. Volterra, *Physica C* **258**, 373 (1996).

[6] N. Jovic, B. Antic, A. Kremenovic, A. Spasojevic de Bire, V. Spasojevic, *Phys. Status Solidi A* **198**, 18 (2003).

[7] A. Kuhn, M. Martin, F. Garcia-Alvarado, *Z. Anorg. Chem.* **634**, 880 (2008).

[8] T. Kanno, J. Awaka, F. Kariya, S. Bisu, S. Nagata, *Physica B* **381**, 30 (2006).

[9] C.P. Sun, Y.F. Huang, S.T. Tai, C.L. Huang, H.D. Yang, *Physica B* **378-380**, 395 (2006).

[10] Z. Zamora, T. Lopez, R. Gomez R, *J. Sol–Gel Sci. Technol.* **32**, 339 (2004).

[11] M. Picquart, L. Escobar-Alarcon, E. Torres, T. Lopez, E. Haro-Poniatowski, *J. Mater. Sci.* **37**, 3241 (2002).

[12] D.D. Claudio, A.R. Phani, S. Santucci, *Opt. Mater.* **30**, 279 (2007).

[13] J. Yang, J. Zhao, Y. Chen, *Ionics* **16**, 425 (2010).

[14] C.Q. Feng, L. Li, Z.P. Guo, D.Q. Shi, R. Zeng, X.J. Zhu, *J. Alloys Comp.* **478**, 767 (2009).

[15] L.H. Yang, C. Dong, H.H Song, J. Guo, G.C. Fu, *Chin. Phys. Lett.* **22**, 243 (2005).

[16] M. Łapiński, B. Kościelska, W. Sadowski, *J. Alloys Comp.* **536**, 30 (2012).

[17] M. Łapiński, B. Kościelska, W. Sadowski, *J. Phys. Chem. Solids* **74**, 575 (2013).

[18] B.V. Crist, *Handbook of Monochromatic XPS Spectra*, Wiley, Chichester 2000.

[19] L.Q. Wang, D.R. Baer, M.H. Engelhard, *Surf. Sci.* **320**, 295 (1994).

[20] F. Guillemot, M.C. Porte, C. Labrugere, Ch. Baquey, *J. Colloid Interf. Sci.* **255**, 75 (2002).

[21] L.B. Xiong, J.L. Li, B. Lang, Y. Yu, *J. Nanomater.* **2012**, 831524 (2012).